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Neutron and X-ray reflectivity analysis of ceramic-metal materials

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Abstract

Neutron and X-ray reflectivity measurements of a thin film of cermet (ceramic-metal) made by co-sputtering Pt and Al_2O_3 on the surface of a flat piece of float glass are presented. From the analysis of the specular and off-specular measurements, the morphology of the Pt clusters which are embedded in the Al_2O_3 matrix is determined by adjusting a model to the observed data. It is found that the structure of such films presents a certain degree of order in the direction normal to the surface of the films but no correlation (or with a very short correlation length not measurable by this technique) in the plane of the film.

Keywords: X-ray scattering; Platinum; Ceramic-metal; X-ray reflectivity

1. Introduction

It is now well established that X-ray and neutron reflectivity experiments are extremely useful to determine the density profile of thin films in the direction normal to their surface. Whereas the number of publications, where X-ray and neutron reflectivity have been used, has been constantly increasing, it is remarkable to notice that most of the work which has been done so far was performed on laterally homogeneous materials. The reflectivity study of materials presenting lateral fluctuations of electron density or strong fluctuations of the density in the direction normal to the surface is now attracting more attention and a theoretical approach of systems presenting various kinds of fluctuations was presented recently by Rausher et al. [1]. Usually heterogeneous materials are studied at small angle of scattering in transmission by small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS). These techniques have however the major drawback of not being very much surface sensitive. The idea to combine both SAXS or SANS with reflectivity measurements to study thin heterogeneous films is therefore very appealing. Examples in which lateral fluctuations of electron density have been studied can be found in various materials such as sputtered Pt [2], the electrochemical pitting of copper [3], LB molecular multilayer thin films [4] or ordered diblock copolymers [5]. In these examples, except for the LB films, all the other materials present islands or holes in their surface which cause the fluctuations of electron density. These fluctuations are then mainly studied by performing scans parallel to the surface of the film. Usually the size and in the very best cases the shape of the islands or holes can be accessed as well as the mean distance between the islands or holes. In a recent paper, Maaza et al. [6] have studied ceramic-metals (cermets) materials which are believed to be composed of small metallic particles inserted in a ceramic amorphous matrix. In cermet, it is expected that the heterogeneity will be found in the entire thickness of the film and not only at the surface. They have shown in an experimental and theoretical way that reflectivity measurements can provide information about the size and the distribution of particles inserted in thin films. However, as the measurements reported in [6] were only made in the specular direction, only the fluctuations in the direction normal to the surface were possibly analyzed. To have a complete understanding of the structure of such films it is therefore important to measure simultaneously both the specular and off-specular components of the reflectivity. We report in this paper a complete study of thin films of cermets by presenting both the neutron and X-ray specular reflectivity and the off-specular scattering results. In particular, we show that the model that was used in [6] remains valid for specular reflectivity but does not explain the off-specular scattering results. An extension of this model is now proposed.

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2. Experimental

Ceramic-metal thin films of Pt/Al_2O_3 were made at the Laboratoire d'Optique des Solides (Paris) by co-sputtering Pt and Al_2O_3 on the surface of a flat piece of float glass or silicon. In this paper, we are focusing on the glass substrate and we will soon report the results obtained on the silicon substrate which appear to be somewhat different.

During the sputtering process the substrate is rotated to ensure that the film will be homogeneous. The concentration of Pt in the films depends on the number of Pt pellets which are deposited on the surface of a Al_2O_3 target when starting the sputtering process; this number was 70 in this case and the diameter of the pellets was 5 mm. In the following, we shall label the sample as $Pt_xAl_2O_3$; we estimate from the critical angle measured in this sample that $x \approx 0.3$. X-ray reflectivity measurements were carried out on a Philips reflectometer operating at 40 kV, 40 mA at the University of Maine (Le Mans). The K_α line was selected by reflection of the scattered beam on the surface of a flat pyrolitic graphite analyzer located between the sample and the detector. The resolution of the instrument was determined by a pair of front slits located in front of the sample and by soller slits located after the sample. The full width at half maximum (FWHM) of the direct beam was 0.065°. Neutron experiments were carried out on the NG7 reflectometer of NIST with a varying collimation to increase the signal over noise ratio. In both cases, the incident and outgoing beams were moving and the sample was kept fixed in a horizontal position (reflectometer in the theta–theta configuration).

3. Theoretical background

As recently shown in reference [6], the intensity which can be measured out of a thin film presenting heterogeneity can be separated into two parts. The first one, R_1, is the contribution of the film interfaces to the reflectivity and can be calculated by assuming an homogeneous film of thickness L having a density ρ_a which is the average electron density of the homogeneous film. The contribution of the heterogeneity, R_2, can be calculated by considering that the center of mass of the particles is located at positions r_i and that the particles have a certain shape which at first can be considered as spherical. If we consider that there is no interaction between the beam reflected by the interfaces and the beam scattered by the metallic grains then the total scattering will be the sum of two terms. The first one will be the reflected intensity by the interfaces and the second one the contribution of the metallic clusters. The electron density due to the clusters at a specific position r in the film is then given by

$$\rho(r) = \left(\rho_{Pt} - \rho_{Al_2O_3}\right)(r) * \sum_i \delta(r - r_i) \quad (1)$$

where $\rho_{Al_2O_3}$ and ρ_{Pt} are the electron densities of the homogeneous film and of the Pt clusters and the sign * stands for the convolution operation.

As shown previously [6], the contribution of the heterogeneity to the scattering is given by the Fourier transform of the autocorrelation function of the electron density that we shall call S_2. To include this contribution to the measured intensity one has to take into account the absorption at very shallow angle of incidence (especially for X-rays). This is done by calculating the penetration depth in the material that we multiply by the imaginary part of the wavevector in the cermet. An exponential correction, E, having this argument is then applied to S_2. A $4/L_xL_yq_z^2$ correction is introduced which takes in account the reflection geometry (L_xL_y is the coherently illuminated area of the beam) and a scale factor A allows to vary the Pt concentration in the cermet. The absolute reflectivity is then given by

$$R = R_F + \frac{4r_0^2}{L_xL_yq_z^2}AES_2 \quad (2)$$

in which R_F is the convolution of R_1 with the resolution function and r_0 is the classical radius of the electron. The second term of the above sum is extremely broad in q_z and therefore does not need to be convolved with the longitudinal part of the resolution function. It can be calculated under the condition to express S_2. This quantity is the product of a form factor *f(Q)* which depends on the shape of the particles by a structure factor *S(Q)* which depends on the interference of the scattered waves by the particles. In [6], it was assumed that the Pt particles were spherical and for this reason the form factor was given by

$$f(Q) = \left(\rho_{Pt} - \rho_{Al_2O_3}\right)^2 \left(\frac{4R^3}{3}\right)^2 \left(\frac{\sin QR - QR\cos QR}{Q^3R^3}\right)^2 \quad (3)$$

The structure factor was obtained by assuming a paracrystalline disorder, as described by Hoseman [7], a disorder which basically leads to:

$$S(Q) = \frac{1 - e^{-2Q^2\sigma^2}}{1 - 2\cos(Qd)e^{-Q^2\sigma^2} + e^{-2Q^2\sigma^2}} \quad (4)$$

in which d is the average distance between first neighbours and σ is the mean standard deviation from this value. In this formalism it was assumed that the particles were isotropically distributed so that the degree of disorder was well defined by the ratio σ/d in all the directions. Another consequence of this assumption is that Q stands for a radial value of the wavevector transfer so that the scattering from the particles should present a radial distribution as for example in a powder. The signature of the presence in the film of spherical particles randomly distributed in the sample lies therefore in the observation of rings of diffraction. Therefore it was interesting to prove the validity of the previous model to check for the presence of off-specular scattering as intense as the specular component at least where the contribution of the particles becomes predominant.

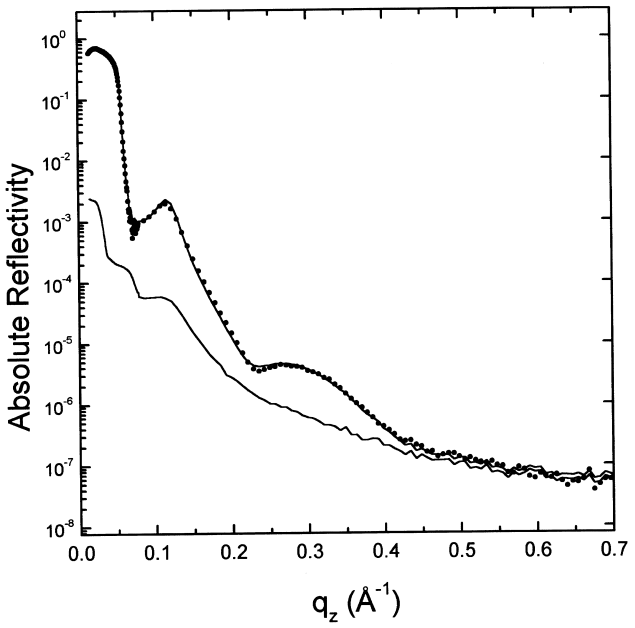

Fig. 1. Observed (circles) and calculated X-ray reflectivity of a $Pt_xAl_2O_3$ cermet. The full line which does not follow the circles is the off-specular reflectivity measured with an off-set of 0.12°.

4. Results

As already reported in [6], the X-ray reflectivity curve shown in Fig. 1 is characterized by the total reflection plateau which is quite rounded up showing that the absorption in the sample is very important. As soon as the critical angle is passed, i.e. for $q_z > ; 0.056$ Å^{-1}, there is a very steep decrease of the intensity which can be expected from an important roughness of the film-air interface. We found that the roughness of this interface is at least 30 Å so that the contribution of the film interfaces to the reflectivity is decreasing extremely fast. A few oscillations are then observed which correspond to the Kiessig fringes. The distance Δq_z which separates the fringes allows to determine the film thickness. This contribution of the film interfaces with air and substrate becomes insignificant around 0.1 Å^{-1} where a predominant hump appears circa $q_z = 0.12$ Å^{-1}. The height of this hump strongly depends on the number of pellets used to prepare the film. Its location depends on the nature of the pellet. We have observed that for silver pellets the hump comes closer to the origin of the wavevector transfer. Therefore there is little doubt that the observation of this hump is related to the presence of the metallic element in the film. The fact that its intensity increases with the number of pellets but that its position is independent of it, strongly supports the idea of a concentration effect. The line-shape of the hump seems to rule out the possible presence of a single metallic layer at the substrate-film interface but is more compatible with what is observed in a multilayer presenting a strong cumulative disorder. We therefore believe that the film presents some stratified regions which are more concentrated in Pt than others. In the previous analysis of the specular reflectivity, the picture of the film [6] was the one of a raisin cake in which the 'Pt raisins' were supposed to be of different size and were isotropically distributed in the Al_2O_3 film. We would like now to focus more on the diffuse scattering to check the validity of this assumption.

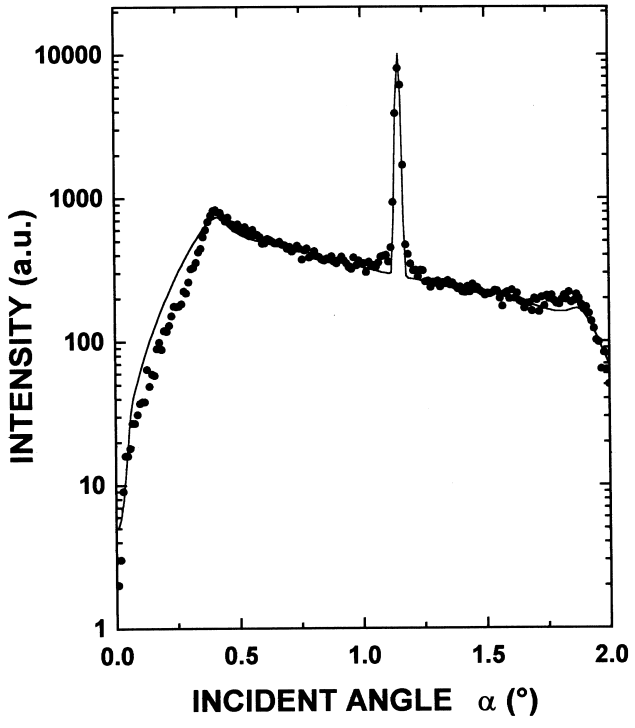

Fig. 2. Transverse scan parallel to the surface of the sample measured with X-rays at the location of the first observed hump. The solid line is a fit to the data which are shown in circles.

The above picture can only be valid if the broad hump is ring-shaped and therefore if this hump which is observed at $Q = 0.12$ Å^{-1} is also visible in any off-specular scans. We surprisingly found as shown in Figs. 1 and 2 that the scattering was composed of a true specular part sitting on a diffuse component weaker by one to two orders of magnitude. In Fig. 1, the diffuse scattering was measured with a 0.12° offset of the incident angle with respect to the specular condition. Transverse scans (rocking curves) parallel to the surface of the sample were also performed to get complementary information about the shape of the diffuse scattering. We found out that the diffuse intensity was essentially flat (at least over the measured interval) in the direction parallel to the surface as shown in Fig. 2. The slight slope observable in Fig. 2 is due to a footprint effect which can be easily accounted for. The two shoulders on each side of the scans are the Yoneda wings. It is very important to notice that although the diffuse scattering is flat, it weights for a large amount of the intensity. The flatness of the diffuse scattering observed in a q_x transverse scan does not evolve very much as a function of the wavevector transfer q_z

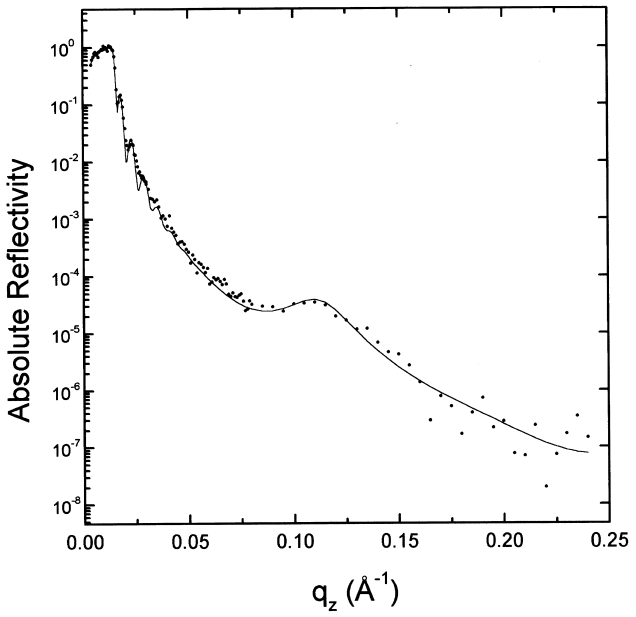

Fig. 3. Observed (circles) and calculated neutron reflectivity of a $Pt_xAl_2O_3$ cermet.

normal to the surface; it remains flat with a slight change in the ratio of the diffuse to specular intensity clearly visible in Fig. 1.

The reflectivity curve obtained from neutron reflectometry shown in Fig. 3 is quite similar to the one obtained from X-ray measurements. However due to the lack of contrast between the Pt and Al_2O_3, the hump is far less pronounced with neutrons but is clearly observable. This also explains that diffuse scattering of neutrons was not observable.

In the view of such results, it is somewhat difficult to consider that the reflectivity can only arise from small spherical particles which are isotropically distributed in the film. The fact that the specular part is quite intense with respect to the diffuse one, seems to point towards the presence of flat reflecting regions inside the film. Those regions must be either quite extended laterally or made from a large number of small flat regions to account for the fact that the specular reflectivity is resolution limited in a transverse scan. Therefore it seems from this work that a system presenting some anisotropy would be more appropriate to interpret the reflectivity curves and the question we wish to address now is how are distributed these flat regions in the film both in the directions parallel and perpendicular to the surface. For this, we have to interpret both the rocking curves and the reflectivity. First, we would like to stress that the reflectivity (i.e. the contribution of the z dependence of the electron density) can be analyzed directly without taking care of the diffuse scattering. This can be done because the diffuse intensity is not peaked at the specular position and is less intense than the specular component so that subtracting the diffuse component from the specular has little effect except at very large q_z wavevector transfer. This also means that in the scattering cross-section, the q_z dependence can be separated from the $q_{//}$ dependence. Second, the fact that the diffuse intensity is essentially flat tells us that the in-plane correlation between Pt clusters is extremely weak at least over long distances (which are easily measurable in this kind of geometry). We next show that if we have a random in-plane distribution of platinum clusters with no correlation at all between the clusters we should expect the scattering in the direction parallel to the surface to be the sum of a delta function which would scale as the square of the clusters number sitting on the top of a flat background scaling as the number of clusters. This is close to what we get from the rocking curve scan shown in Fig. 2.

5. A modified model

In order to describe our experimental data, we proposed a modified version of the model presented in [6] which now takes into account the anisotropy of the scattering. The distribution of the heterogeneity is based on the following assumptions

- there is a degree of ordering of the Pt clusters in the direction normal to the surface. This degree is consistent with a cumulative disorder as described in the Hoseman model [7]. This assumption leads to the fact that Q in the previous model must be replaced by q_z.
- there is no lateral correlation between the *Pt* regions in the plane of the film surface or if a correlation exists the range over which it extends is not accessible (in particular the geometry of the experiment does not allow the determination of very small correlation lengths $\sim <$ 70 Å)
- due to the finite thickness of the film the number of Pt clusters along the z direction is far less than in the plane of the film.
- it is assumed that the clusters lie on the average in planes parallel to the plane of the substrate

As a result, the electron density which corresponds to the heterogeneity becomes

$$\rho(r) = \left(\rho_{\mathrm{Pt}} - \rho_{\mathrm{Al_2O_3}}\right)(r) * \sum_i \sum_k \delta(r - r_{ik}) \tag{5}$$

where the index i stands for the position along the z axis and the label k for the position in the plane of the surface. The position of any cluster with respect to an arbitrary origin becomes

$$r_{ik} = z_i + u_k^i \tag{6}$$

The intensity scattered by the heterogeneity is obtained by Fourier transform of the autocorrelation function of the function defined in Eq. (5). We further assume that the correlation between clusters is extremely weak in the plane of the surface as inferred from Fig. 2 and in addition that this correlation does not depend on the altitude of a cluster (hypothesis of stationarity). If we call u the variable

Table 1
The parameters used to fit the X-ray reflectivity data

Film thickness	830 ± 2 Å
Air–film roughness	40 ± 3 Å
Substrate–film roughness	5 Å
Critical q_c of the film	0.056 ± 0.002 $Å^{-1}$
Average neighbouring distance between the center of mass of two clusters along the z direction	53 ± 8 Å
Average cluster thickness along the z direction	28 ± 3Å

defining the in-plane location, the above assumption yields

$$\sum_{i,j} \delta\left(u - \left(u_i^1 - u_j^1\right)\right) = \sum_{i,j} \delta\left(u - \left(u_i^2 - u_j^2\right)\right) \quad (7)$$

The calculation of the autocorrelation function is a bit tedious except if one consider that the above assumptions allow to completely separate the z and u variables. After performing the calculation, the Fourier transform of the interference term becomes

$$S(Q) = N_3 \frac{1 - e^{-2q_z^2\sigma^2}}{1 - 2\cos(q_z d)e^{-q_z^2\sigma^2} + e_z^{-2q}2\sigma^2} \times N_1 \frac{1 - e^{-2q_{//}^2\sigma_{//}^2}}{1 - 2\cos(q_{//}d_{//})e^{-q_{//}^2\sigma_{//}^2 + e_{//}^{-2q^2}\sigma_{//}^2}} \quad (8)$$

in which $q_{//}$ is the component of the wavevector transfer in the plane of the film, $d_{//}$ is the correlation length in the plane of the interfaces and N_1 is the number of particles which is coherently illuminated in the plane of the film. In the limit where the in-plane correlation is extremely weak, the last term of Eq. (8) yields

$$N_1^2 \delta q_{//} + N_1 \quad (9)$$

showing that one should expect a constant intensity in any off-specular scan (q_x scan) dominated by sharp component in the specular. A similar result could have been obtained directly as shown for example in the book of De Coulon [9]. This result is also a classical result of what can be expected from a random distribution of clusters. In the limit where q_z is large compared to the critical q_c of the film, we expect from the above model that the diffuse intensity will follow the same q_z behaviour than the sharp specular component. However the intensity of the sharp component will scale as N_1 square and the diffuse one as N_1. We thus expect that the ratio between the specular and diffuse intensities will be N_1 and will depend on q_z since N_1 is the number of clusters which is coherently illuminated by the beam. This number depends on the incident angle of the beam with respect to the surface of the sample and is thus q_z dependent. This dependence can be taken in account but the out of plane resolution is also affecting the result so that we have not yet found a simple expression of the exact evolution of this ratio as a function of q_z.

The above model was fitted to the specular data and the result of the fit is presented in Fig. 1 (solid line). The calculation was made into two steps; first the plateau region and the steep decrease were calculated via the matrix technique assuming a homogeneous thin film on top of the substrate. From this calculation we extracted the film thickness and the roughness of the interfaces. The contribution of the particles was then added to the reflectivity of the thin film and the diffuse part was finally added to take in account a fluctuating background. One can clearly see that the above model describes the experimental data fairly well. The calculation was performed in the same way to analyze the neutron data shown in Fig. 3 and the only parameter we changed was the scale factor and the scattering length density of the materials. The parameters of the fit are reported in Table 1. The transverse scan of Fig. 2 was also calculated according to expression 9. One can clearly see that there is a narrow component and a flat background. The Yoneda wings (i.e. the two shoulders on each side of the scan) are described in the distorted Born approximation by multiplying the scattering cross-section by the usual coefficient T_1 and T_2 defined in [8]. In the transverse scan of Fig. 2 in which the incident angle α of the direct beam is varied with respect to the surface of the film and for which the detector is kept at the fixed position $2\theta = 2.3°$, we find that these coefficients are peaked at the angles $\alpha = \alpha_c = 0.43°$ (incident angle) and $\alpha = 2\theta - \alpha_c = 1.89°$. The location of the Yoneda peaks is thus in agreement with an average critical angle which is intermediate between the one of pure Pt $\alpha_c = 0.58°$ and the one of pure alumina which is $\alpha_c = 0.29°$. The transformation of the critical angle in terms of critical wavevector leads to a value of 0.061 $Å^{-1}$ which can be compared to the value of 0.056 $Å^{-1}$ for the homogeneous film. There is a slight difference between these two values which is not completely understood except by the fact that the Yoneda peaks are simulated according to a model of a homogeneous film and that this is clearly not the case. It can be also observed that the decay of the scattered intensity is not ideally reproduced beyond the Yoneda peaks especially at very shallow angle of incidence.

6. Conclusion

We have shown in this experimental study of Pt-Al_2O_3 ceramic-metal thin films that the structure of such films is anisotropic. If it is clear that along to the surface normal (z direction) the structure presents a certain periodicity which consists of blocks of Pt 28 Å thick separated by an average distance of 53 Å, there is a clear evidence from our off-specular scattering measurements that there is no correlation at all (or with a very short correlation length $\ll$, Format: = True100 Å) between these blocks in the direction parallel to the surface. In the plane of the film and with geometry used

in this experiment, the blocks appear to be located at random. This randomness gives rise to a delta function in the transverse scans parallel to the surface of the sample and to an important background which is essentially flat. The interpretation of the structure of heterogeneous thin films is presently a challenge due to the complexity of these films. This study gives a possible way of analysis of such films according to an analytical model which, as every model has its limitation. In this case we rely on a starting guess of the structure and we refine a few parameters to adjust the model to the reflectivity measurements. The solution is not in principle unique and one must be confident in the starting guessed model. A further step in the interpretation of the structure of such films could be achieved by using complementary techniques such as transmission electron microscopy to have a direct view of the granularity. An other alternative is to perform grazing incidence small angle X-ray scattering (GISAXS) measurements as recently reported by Naudon et al. [10,11] to get a better understanding of small correlation lengths; this will be done soon. As also pointed out at the beginning of this paper, it seems that the nature of the substrate is of great importance in the profile of the observed humps. This clearly shows that the granularity can be different from one film to one another according to the conditions of sputtering. These aspects will be soon discussed in a following paper.

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